

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 074-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY		2. REPORT DATE 6/29/98		3. REPORT TYPE AND DATES COVERED Technical Report, Oct 1996 - June 1998
4. TITLE AND SUBTITLE A Mechanistic Study of the Influence of Proton Transfer Processes on the Behavior of Thiol/Disulfide Redox Couples				5. FUNDING NUMBERS N00014-96-1-0673 96PR0-3839
6. AUTHOR(S) E. Shouji and D. A. Buttry				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Wyoming Laramie, Wyoming 82071-3838				8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report 38
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, ONR 331 800 North Quincy Street Arlington, VA 22217-5660				10. SPONSORING / MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES Prepared for publication in <i>Journal of Physical Chemistry B</i>				
12a. DISTRIBUTION / AVAILABILITY STATEMENT This document has been prepared for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 Words) The mechanism of the oxidation of 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT) to its disulfide dimer (BMT) and its subsequent reduction has been examined with a combined approach employing experimental data and digital simulation. In order to elucidate the influence of proton transfers on these redox processes, special attention has been paid to the influence of various bases, including triethylamine, pyridine, 3-chloro-pyridine, lutidine and 2,6-di- <i>tert</i> -butyl-pyridine, and proton donors, including methanesulfonic acid and trifluoromethanesulfonic acid, on both the oxidation and reduction reactions. Based on detailed comparisons of the experimental data with simulations of several mechanistic models, it is found that proton transfer pathways have a pronounced influence on both the oxidative and reductive pathways. In particular, McMT oxidation is facilitated by a rapid bimolecular proton transfer from McMT to weak bases such as Py that produces McMT ⁺ , the thiolate form, which is then oxidized. The overall kinetic scheme by which these redox processes proceed both in the presence and absence of proton transfer agents is discussed, especially with regard to the potential use of a related dithiolate compound as a cathode material in Li secondary batteries.				
14. SUBJECT TERMS sulfur compound electrochemistry, simulation, mechanism				15. NUMBER OF PAGES 22
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT unclassified NSN 7540-01-280-5500	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT	
			Standard Form 298 (Rev. 2-89) Prescribed by ANSI Std. Z39-18 298-102	

19980710 050

OFFICE OF NAVAL RESEARCH

GRANT # N00014-91-J-0201

R&T CODE: 4133032

Technical Report No. 38

A Mechanistic Study of the Influence of Proton Transfer Processes on the Behavior of Thiol/Disulfide
Redox Couples

E. Shouji and D. A. Buttry

Prepared for publication

in

Journal of Physical Chemistry B

Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071-3838

June 29, 1998

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

REPORT DOCUMENTATION PAGE

2. June 29, 1998

3. Technical Report

4. "A Mechanistic Study of the Influence of Proton Transfer Processes on the Behavior of Thiol/Disulfide Redox Couples"

5. GRANT: N00014-96-1-0673, PR # 96PRO-3839

6. E. Shouji and D. A. Buttry

7. Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

8. Org. Report # - none

9. Office of Naval Research, Chemistry Division, 800 N. Quincy Street, Arlington, VA 22217-5660

10. Technical Report No. 38

11. Submitted to: *Journal of Physical Chemistry B*

12. Unlimited distribution

13. Abstract: The mechanism of the oxidation of 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT) to its disulfide dimer (BMT) and its subsequent reduction has been examined with a combined approach employing experimental data and digital simulation. In order to elucidate the influence of proton transfers on these redox processes, special attention has been paid to the influence of various bases, including triethylamine, pyridine, 3-chloro-pyridine, lutidine and 2,6-di-*tert*-butyl-pyridine, and proton donors, including methanesulfonic acid and trifluoromethanesulfonic acid, on both the oxidation and reduction reactions. Based on detailed comparisons of the experimental data with simulations of several mechanistic models, it is found that proton transfer pathways have a pronounced influence on both the oxidative and reductive pathways. In particular, McMT oxidation is facilitated by a rapid bimolecular proton transfer from McMT to weak bases such as Py that produces McMT⁻, the thiolate form, which is then oxidized. The overall kinetic scheme by which these redox processes proceed both in the presence and absence of proton transfer agents is discussed, especially with regard to the potential use of a related dithiolate compound as a cathode material in Li secondary batteries.

15. Number of Pages: 22

16. Price Code: UL

17. 18. 19. Unclassified

20. Limitations: UL

A Mechanistic Study of the Influence of Proton Transfer Processes on the Behavior of Thiol/Disulfide Redox Couples

Eiichi Shouji and Daniel A. Buttry *

*Department of Chemistry, University of Wyoming, Laramie, Wyoming,
82071-3838, USA*

Email: Buttry@Uwyo.edu; FAX: (307) 766-2807

Abstract

The mechanism of the oxidation of 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT) to its disulfide dimer (BMT) and its subsequent reduction has been examined with a combined approach employing experimental data and digital simulation. In order to elucidate the influence of proton transfers on these redox processes, special attention has been paid to the influence of various bases, including triethylamine, pyridine, 3-chloropyridine, lutidine and 2,6-di-*tert*-butyl-pyridine, and proton donors, including methanesulfonic acid and trifluoromethanesulfonic acid, on both the oxidation and reduction reactions. Based on detailed comparisons of the experimental data with simulations of several mechanistic models, it is found that proton transfer pathways have a pronounced influence on both the oxidative and reductive pathways. In particular, McMT oxidation is facilitated by a rapid bimolecular proton transfer from McMT to weak bases such as Py that produces McMT⁻, the thiolate form, which is then oxidized. The overall kinetic scheme by which these redox processes proceed both in the presence and absence of proton transfer agents is discussed, especially with regard to the potential use of a related dithiolate compound as a cathode material in Li secondary batteries.

*) To whom correspondence should be addressed

Introduction

The potential use of 2,5-dimercapto-1,3,4-thiadiazole (DMcT, see Scheme 1) as part of a composite cathode material for secondary lithium batteries ¹ has prompted a flurry of both spectroscopic and electrochemical investigations of the redox processes of this compound and several of its derivatives. ¹⁻⁷ A particularly interesting aspect of the behavior of DMcT is the apparent facilitation of its oxidative polymerization and reductive depolymerization by poly(aniline) (PAn). ¹⁻⁷ In fact, the cathode materials that have been shown to have very attractive energy densities ¹ and rapid charging characteristics ³ have been based on molecular level composites of DMcT and PAn, sometimes with other additives present. ³ This facilitation of the DMcT redox process comprises an important finding, because, even though the thermodynamics of thiol/disulfide redox processes are quite attractive from the perspective of lithium cathode materials, their kinetics are typically very slow at room temperature. ⁸ Thus, gaining an understanding of the mechanism by which PAn accelerates the DMcT redox transformations is likely to be very worthwhile. While the mechanism of this facilitation has yet to be elucidated, previous results have suggested that proton transfer processes can have a strong influence on both the kinetics and thermodynamics of the thiol/disulfide redox couple. ⁷ In order to explore this issue in more detail, we have begun a detailed series of studies of the redox chemistry of thiadiazole systems bearing thiol substituents in the presence of various acidic and basic

proton transfer agents.⁷ Given that oxidation of the dithiol systems, such as DMcT, results in polymerization and precipitation on the electrode surface, which leads to “phase-like” behavior and consequent deviations of the redox responses from theoretical expectations,⁹⁻¹¹ we have chosen to study the behavior of 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT, see Scheme 1) as a model system, which has been briefly examined previously.^{4,5,7} As will be seen below, this compound is oxidized to give a disulfide dimer in a well-behaved, quasi-reversible redox process. Thus, it provides a suitable couple for detailed comparison of experimental data with the results of digital simulations.

In constructing a kinetic scheme that satisfactorily describes the influence of proton accepting bases on the redox behavior of McMT, it has been necessary to provide several thermodynamic and kinetic parameters as inputs for the digital simulation. As far as possible, these parameters have been obtained from a thorough survey of the literature. For example, an important reaction in the simulation is the coupling reaction of two RS• radicals to produce the RSSR disulfide species. This type of reaction has been studied previously,^{12,13} and the rate constant has been found to be large. Thus, as will be seen below, a value of $10^6 \text{ M}^{-1} \text{ s}^{-1}$ was used in the simulation. Another reaction whose kinetics have a strong influence on the simulation is the reduction and subsequent cleavage of the SS bond in the disulfide dimer. In this case, spectral observations^{12,13} of the RSSR^{•-} intermediate, which decomposes to RS⁻ and RS•, verify that the reduction occurs via a stepwise, rather than concerted, pathway,¹⁴ and that the rate constant for the heterolytic dissociative cleavage of RSSR^{•-} is $> 10^5 \text{ M}^{-1} \text{ s}^{-1}$. For this process, a value of $10^7 \text{ M}^{-1} \text{ s}^{-1}$ was used in the simulation. For cases in which acid-base chemistry is important, values of pK_a's for the various species in non-aqueous solvent systems have been used wherever possible.¹⁵⁻²⁰ In particular, a well established correlation²⁰ between the pK_a's of radical cations of thiol species, the pK_a of the parent thiol, and the difference in oxidation peak potential for the thiolate anion and the thiol has been used to estimate the pK_a of the radical cation of McMT. Finally, since proton transfer to and from heteroatoms and heteroatomic cation radicals is typically quite fast,^{21,22} fairly large values for the rate constants for such proton transfer reactions were used. We will return to a more thorough discussion of the various kinetic and thermodynamic values used as inputs for the simulation below.

An additional consideration about the use of simulations to model such processes relates to the fact that the simulation requires that the redox processes be treated as a series of elementary steps. Thus, for example, in the reduction of a species such as RSSR, each of the two electron transfers that ultimately will produce two equivalents of RS⁻ must be expressed and calculated separately within the simulation, along with any intermediate chemical reactions that are thought to occur along the reaction pathway. In many cases, the sequence of elementary steps used in the simulation can be combined in a thermodynamic cycle^{20,23,24} to construct the overall reaction. For example, for RSSR reduction the overall reaction would be:



while the elementary steps would involve reduction of RSSR by one electron, its subsequent dissociation to give RS^- and RS^\cdot , and the subsequent reduction of the radical to give RS^- or its dimerization to give RSSR, which will itself be reduced, etc. Because these elementary steps are thermodynamically interrelated, their equilibrium constants (for chemical reactions) and E° 's (for electrochemical reactions) cannot be varied independently, providing some constraints on the number of independent variables in the simulation.

Experimental Section

Materials. Acetonitrile (AN) was purchased from Aldrich Chemical Inc., purified by distillation from P_2O_5 , and stored over 3Å molecular sieves. McMT was purchased from Aldrich Chemical Inc. and was used after recrystallization from AN. 3-chloro-pyridine, pyridine, lutidine, 2,6-di-tert-butyl-pyridine and triethylamine were also purchased from Aldrich Chemical Inc. and were used after purification by distillation. Deuterated acetonitrile (AN- d_3) for NMR measurements was used as purchased from Aldrich Chemical Inc.

Electrochemical Measurements. Cyclic voltammograms were obtained at 25 °C using a BAS CV-27 and a Hewlett-Packard 7045B xy recorder. Measurements were taken in a three electrode cell configuration using a glassy carbon disk electrode (Cypress Systems, Inc., 3.0 mm diameter), a Pt coil (0.5 mm diameter, 50 cm length), and a Ag/AgCl reference electrode, against which all potentials are reported. Unless otherwise noted, all experiments were conducted in a 0.1 M $LiClO_4$ AN solution, which was extensively deaerated using nitrogen gas, and at a scan rate of 50 mV s^{-1} .

Spectroscopic Methods. UV-vis spectra were recorded using Hewlett-Packard HP8452 diode array spectrometer in AN solution. IR spectra in AN solution were recorded using a Bomem MB100 spectrometer (MCT detector, resolution of 1 cm^{-1}) in AN solution with the solution placed between two KBr crystals (25 mm diameter, 5 mm thickness). Raman spectra were recorded using a Spectra-Physics Stabilite 2017 Ar ion laser (514.5 nm) and a SPEX 270M single monochromator with a Spectrum One CCD detector. NMR spectra were recorded using a JEOL NMR-270 MHz in AN- d_3 solution. Considerable care was taken to ensure the exclusion of both oxygen and water from the samples during these experiments.

Digital Simulations. Simulations of cyclic voltammograms²³ were done using Digisim Ver. 2.1 (Bioanalytical Systems, Inc.) with a personal computer (Pentium 200MHz Pro, Windows95). The following model parameters were used: exponential grid factor: 0.5, potential step: 5×10^{-3} V, and noise level: 0 A, temperature: 25°C, scan rate: 50 mV s^{-1} and diffusion coefficient = 1×10^{-5} cm^2/sec . Pre-equilibrium was enabled for chemical reactions only.

Results and Discussion

Redox Behavior of the Disulfide Dimer. Scheme 1 shows the structures of McMT, its thiolate form (McMT⁻) and the disulfide dimer (BMT) formed by oxidation of either one of these species. Simulation of the McMT/BMT system is complicated by the acid-base and other chemistry that can follow the redox processes. For example, McMT oxidation produces the radical cation species $McMT^{\cdot+}$, which can deprotonate, producing the $McMT^\cdot$

radical which can then dimerize via radical-radical coupling. On the other hand, reduction of BMT initially produces $\text{BMT}^{\cdot-}$, which will dissociate to produce $\text{McMT}^{\cdot-}$ and $\text{McMT}^{\cdot-}$, which itself can either be reduced to McMT^- or dimerize with another $\text{McMT}^{\cdot-}$ to generate more dimer, followed by its reduction, etc. Thus, the overall mechanisms of these redox transformations involve several reactions, some of which are thermodynamically related (see above). In order to minimize the number of independent variables initially employed in the simulations, we begin by examining the simplest redox process, reduction of BMT to produce McMT^- and its subsequent reoxidation back to BMT. As will be seen, this transformation can be treated using a set of four equations, three of which are independent. After using the simulation to fit this simple case, we will increase the level of complexity by including the proton transfer reactions necessary to model the reactions involving acids and bases.

Figure 1a shows a cyclic voltammogram (CV) of a 10 mM solution of BMT. The upper curve, which gives the experimental result, shows a reduction peak at ca. -0.4 V and a corresponding oxidation peak at ca. 0.0 V. These correspond to the reduction of BMT to give two equivalents of $\text{McMT}^{\cdot-}$, and the subsequent oxidation of $\text{McMT}^{\cdot-}$ back to BMT, respectively. The lower curve gives the simulated result for this case. The elementary reactions required to generate this CV are shown in Table 1, and comprise reactions 2e, 3e, 1c, and 3c. The redox potentials, equilibrium constants and rate constants used to produce the simulated curve are as shown. Note that these four equations are connected by the following relationship:

$$(K_{1c} K_{3c})^{-1} = \exp[(nF/RT) (E_{3e} - E_{2e})] \quad (2)$$

where n = one electron, $F = 96485 \text{ C mol}^{-1}$, and the other quantities have their usual meaning. Thus, only three of these equations are independent. Feldberg and coworkers have discussed the methods by which such thermodynamically superfluous reactions (TSR's) are identified and properly constrained within the simulation.²⁴

It is evident from the figure that the simulation reasonably reproduces the essential features of the experimental data. The values provided in the table for reactions 2e, 3e, 1c and 3c produce an acceptable fit to the experimental CV. Other possible combinations of parameters can also provide acceptable fits to this simple case. However, as will be seen below, while these other combinations cannot be simultaneously used to fit more complex situations, the same kinetic and thermodynamic parameters shown in Table 1 for reactions 2e, 3e, 1c and 3c can be used as part of the fit for the more complex cases involving proton transfer, so long as the appropriate acid-base reactions are included.

Note that the simulation requires two, separate redox processes to reproduce the CV. One is the $\text{McMT}^{\cdot-}/\text{McMT}^-$ redox couple, and the other is the $\text{BMT}/\text{BMT}^{\cdot-}$ redox couple. It is sensible that different E^0 's are used for each of these, since the redox potentials for these two couples should be related to the HOMO of $\text{McMT}^{\cdot-}$ and the LUMO of BMT. This general approach is consistent with many previous studies of the relationship between E^0 's and molecular orbital energies.²⁵ Of course, the peak positions in

the CV are also influenced by the rates of the chemical reactions that follow the initial electron transfer event and by the heterogeneous electron transfer rate constants (k_s values), as given in Table 1.

Redox Behavior of McMT and McMT[•]. Figure 1b shows the experimental (upper) and simulated (lower) cyclic voltammograms for McMT oxidation. As can be seen, McMT is oxidized with a peak potential at +0.95 V, producing an oxidized product that is subsequently reduced at ca. 0.1 V. Previous work has shown that this oxidation produces the disulfide dimer, BMT, (see Scheme 1) and that reduction of the dimer regenerates the thiol.^{4,5} We have recently obtained a crystal structure of the McMT disulfide dimer that unambiguously verifies it as the product of the oxidation.²⁶ Note that, under the conditions in Figure 1a, protons are released to the AN solution as a consequence of the oxidation. Comparison of the peak potentials for reduction of the BMT disulfide dimer in the experimental curves in Figures 1a (-0.35 V) and 1b (0.1 V) reveals that the availability of these protons strongly influences the potential of the reduction process.

Successful simulation of the McMT redox process requires that several additional reactions be included in the model. These are given in Table 1 and comprise: 1e, which describes the oxidation of McMT to McMT^{•+}; 4c, which describes deprotonation of McMT^{•+} to produce a "free" proton and McMT[•] radical; 5c, which describes a rapid pre-equilibrium that produces small amounts of protonated BMT; 4e, which describes the reduction of this protonated dimer; 6c, which describes the rapid heterolytic cleavage of the reduced, protonated dimer to give McMT[•] radical and McMT; and 2c, which describes the protonation of McMT[•] to regenerate McMT. It should be particularly noted that reactions 4e, 5c and 6c were essential to successfully simulating the experimental CV. Various mechanisms using other reactions were investigated, but with no success. Specifically, one such mechanism that was exhaustively investigated involved rapid protonation of the reduced dimer (*i.e.* $H^+ + BMT^{\cdot-} \rightarrow HBMT$) followed by rapid cleavage of this species to give McMT and McMT[•]. Under no circumstances was it possible to simultaneously produce acceptable fits for the CV's in Figures 1a and 1b using a mechanism of this type.

This pre-equilibrium protonation prior to the reduction of the BMT dimer is conceptually quite similar to the square schemes that are used to describe the reduction of systems such as benzoquinone in the absence and presence of proton donors.²⁷ As is the case here, the reduction is facilitated by a proton transfer to the electron acceptor prior to the reduction step. Further, the change in redox potential that occurs on protonation is similar in the present case and that of benzoquinone²⁷ (E^0 for quinone reduction shifts ca. 0.5-0.9 V less negative on protonation, depending on conditions). Thus, the use of reaction 4e is well preceded in the literature concerning the influence of proton donors on reduction potentials.

To further examine the proton-facilitated reduction pathway represented by reactions 4e, 5c and 6c we examined the influence of strong proton donors on the reduction of BMT. Figure 2 shows the voltammetry that is observed for BMT in the

presence of trifluoromethanesulfonic acid (TFA). As TFA is successively added to the solution, one observes an increase in the proton-facilitated reduction wave at ca. 0.1 V. For molar ratios of TFA/BMT less than two, this increase is directly proportional to the TFA concentration. In addition, after traversing this reduction wave, one also observes a new oxidation process at 0.85 V that is characteristic of McMT oxidation (see Figure 1b). This is as expected, since BMT reduction in the presence of protons will produce McMT. Note that the initial scan in all of these cases was in the positive direction, showing that McMT is produced only after BMT reduction in the presence of H^+ . Figure 3 shows the simulation of these cases, in which addition of TFA is modeled by introducing "free" H^+ into the solution prior to the voltammetry. It is significant that none of the kinetic or thermodynamic parameters that were used for simulating the McMT case have been changed. As can be seen, the agreement between the experimental data and the simulation is quite good, suggesting the generality of the reaction pathway embodied in reactions 4e, 5c and 6c in Table 1.

As a further test of the mechanism used in the simulation of the McMT redox system, the influence of addition of a strong base to a solution of McMT was examined. Figure 1c shows the result of addition of one half molar equivalent of triethylamine, TEA, to a solution of McMT prior to the voltammetric experiment. Based on the aqueous pK_a values for TEA²⁸ and McMT⁴ of 10.7 and 5.35, respectively, as well as the results of previous experiments,⁷ one expects that TEA should fully deprotonate 50% of the McMT, in this case producing a solution that is 5 mM in McMT and 5 mM in McMT⁻. The experimental CV (upper curve) shows a redox response characteristic of a 5 mM solution of McMT⁻ (i.e. the BMT/McMT⁻ redox couple, as in Figure 1a) centered at ca. -0.1 V, as well as the oxidation of the remaining 5 mM McMT, in accord with expectations. It is interesting that no reduction peak at 0.1 V for the proton-facilitated reduction of the BMT disulfide dimer is observed when the molar ratio of TEA/McMT is greater than or equal to 0.5. This is because the protons that are produced by McMT oxidation are rapidly consumed by protonation of McMT⁻ that is arriving by diffusion from solution. Thus, the proton facilitated pathway for reduction of the dimer at 0.1 V is not available.

The simulation of the TEA case is shown in Figure 1c (lower curve). Successful simulation of this case required the inclusion of reaction 7c, which describes the protonation reaction for the base. The K_{eq} value for this reaction in the Table was assigned a value of 10^{16} , which is sufficient to cause McMT to protonate essentially all of the TEA that is present, provided the TEA/McMT ratio is less than one. Note that the elimination of the proton-facilitated reduction peak at 0.1 V when TEA/McMT > 0.5 is successfully modeled by the simulation. The voltammetric responses for several other experimentally examined molar ratios of TEA/McMT were also successfully modeled using the same set of simulation parameters.

Before proceeding with a description of the influence of weak bases on the redox behavior of McMT, it is worth briefly discussing the significance of the pK_a values that are used in the simulation. Since the experiments were done in AN solution, these values are referenced with respect to the stability of the proton in AN.¹⁵ The pK_a 's used in the

simulation for the conjugate acids of TEA and the pyridine bases (see below) have been chosen based on previously reported values in AN, DMSO and other non-aqueous solvents,^{15,18,29,30} and are assigned the following pK_a values in AN: TEA (16), lutidine (10), pyridine (8.7), 2,6-di-*tert*-butyl-pyridine (8.7) and 3-chloro-pyridine (7.5). Based on a previous experimental observation⁷ that, for this series of bases in AN solution, McMT is deprotonated only by TEA, McMT has been assigned a pK_a of 13 in the simulation, midway between the TEA and lutidine values. In contrast, some of the species required for the mechanism employed in the simulation are very strongly acidic. For example, reactions 4c and 5c refer to protonation reactions in which very weak bases (McMT[•] and BMT, respectively) are partially protonated by "free" protons in AN. However, these free protons are actually solvated by acetonitrile. Thus, pK_a values of 1 and -0.3 for McMT⁺⁺ and HBMT⁺, for reactions 4c and 5c, respectively, imply that the conjugate bases of these species have basicities comparable to that of AN, which is ca. -10 on an aqueous scale.²⁸ In comparison, a pK_a value for McMT of 13 implies that it is ca. 12 orders of magnitude less acidic than its cation radical, McMT⁺⁺. Bordwell et al.²⁰ have discussed the relative acidities of thiols (pK_{HA}) and their cation radicals ($pK_{HA^{++}}$), and have proposed a correlation that can be used to critically examine the values that have been used in the present simulations. Briefly, they proposed the following relationship:

$$pK_{HA^{++}} = pK_{HA} + 16.8[E_{ox}(A^{\cdot-}) - E_{ox}(HA)] \quad (3)$$

where $E_{ox}(A^{\cdot-})$ and $E_{ox}(HA)$ are the oxidation peak potentials for the thiolate and thiol, respectively, which in the present case are McMT[•] and McMT. They used this correlation to estimate the pK_a values for the cation radicals of 15 thiol compounds. The results were found to be quite satisfactory, with an uncertainty of ca. ± 2 pK_a units.²⁰ Based on the experimentally observed peak potentials for McMT[•] and McMT and the pK_a of McMT that was used in the simulation (13, see above), this relationship predicts that the pK_a of McMT⁺⁺ should be 1.3 (± 2). This reasoning was used to assign a value of 1.0 to this species in the simulation. This discussion shows that the quantitative treatment of the acid-base chemistry of the various species in the simulation is both internally consistent and consistent with the existing literature.

Redox Behavior of McMT in the Presence of Weak Bases. Figure 4 shows the behavior that results when increasing amounts of pyridine are added to an AN solution containing McMT. One observes the appearance of a new oxidation peak at ca. +0.55 V and a corresponding reduction at ca. -0.3 V. These two new peaks shift slightly in the positive direction and increase in intensity linearly with the concentration of pyridine up to the point at which it becomes equimolar with McMT, after which the voltammetry does not change significantly. Corresponding decreases in the peaks due to the McMT/McMT⁺⁺ redox couple are also observed. Note that the peak at 0.1 V for the proton-facilitated reduction of the dimer is not observed above a molar ratio of Py/McMT of 0.5, as was the case for TEA. In this case, this is caused by consumption of the free (AN-solvated) protons by protonation of Py that is supplied by diffusion from bulk solution.

Before discussing the preferred interpretation of these results, it should be pointed out that they are *not* consistent with stoichiometric deprotonation of McMT by pyridine (Py) to produce bulk McMT⁻ prior to the redox process. This is made clear by comparison of Figure 4 with Figures 1a and 1c, which show the redox behavior of the McMT/BMT redox couple. The new response observed in the presence of Py is definitely not the same as that observed for the McMT/BMT redox couple. Further, previous uv-vis spectral studies have demonstrated that Py is not a sufficiently strong base to deprotonate McMT.⁷ To corroborate these findings, NMR studies³¹ of the McMT/Py system were conducted. Figure 5 shows the NMR spectra that are observed for solutions of McMT (curve a), Py (curve c), McMT/Py (curve b), and Py/MSA (curve d, in which the pyridinium cation is produced). Comparison of curves b and d clearly demonstrates that the pyridinium cation is not produced in solutions of McMT/Py, even when Py is present in molar excess. We have also used FTIR³² and Raman³³ spectroscopies to examine this system. In all cases, solutions of McMT and Py were found to contain only the parent compounds; pyridinium could not be detected in any case. Similar experiments were also done to test for stoichiometric proton transfer between McMT and the other pyridine derivatives used in this study, and no evidence for stoichiometric deprotonation of McMT by any of them was observed. Thus, the voltammetric responses shown in Figure 4 are most definitely not due to bulk, stoichiometric production of McMT⁻.

Figure 6 shows the simulated CV for the same set of conditions as in Figure 4. Quite good agreement between the experimental data and the simulation is observed. Exhaustive tests of the simulation using a wide range of values for the various reactions showed that successful simulation of these cases required the inclusion of two additional reactions beyond those that have already been discussed. Specifically, reactions 8c and 9c must be included in order to achieve an acceptable agreement between the experimental data and the simulation. These reactions are TSR's because the acidity and basicity of the proton donors and acceptors in these reactions are defined in reactions 2c, 4c and 7c. Thus, the equilibrium constants for these reactions are not adjustable in the simulation. On the other hand, the rate behavior can be adjusted. Based on previous descriptions of rapid proton transfer in related systems,^{21,22} relatively rapid proton exchange is assumed for these equilibria as reflected in the rate constants used in Table 1.

Detailed examination of the concentration profiles for the various species in the simulation reveals that the primary manner in which reactions 8c and 9c affect the simulation is by providing a rapid pathway through which McMT⁻ can be produced. Thus, reaction 8c provides a rapid pathway for McMT⁻ production, so that it can be oxidized at potentials less positive than those required for direct oxidation of McMT. Reactions 8c plus the reverse of 2e essentially represent a C_rE_i process (*i.e.* reversible chemical reaction followed by an irreversible electrochemical reaction) in the electrochemical notation.³⁴ In addition, reaction 9c drives the formation of McMT⁻, which then couples rapidly to form BMT. Both processes contribute to the new peak at ca. 0.55 V, which is nearer the McMT⁻ oxidation potential. In this case, the shape of the response is characteristic of a C_rE_i case in which the preceding chemical reaction is rapid enough to maintain equilibrium at the scan rate employed.³⁴ It is worth noting that the thermodynamically identical

pathway comprising the reverse of reaction 2c (*i.e.* McMT dissociation to $\text{McMT}^- + \text{H}^+$) and reaction 7c (*i.e.* Py protonation) does not produce simulated results that fit the experimental data. This is because the "unassisted" dissociation of McMT is very unfavorable in AN solution. Thus, even though this overall process can produce sparing amounts of McMT^- in a thermodynamic sense, it cannot produce them rapidly enough to lead to the new oxidation at 0.55 V, given reasonable values for the rate constants for reactions 2c and 7c. This suggests that the rapid production of McMT^- that is responsible for the new peak at 0.55 V in Figure 4 is due to a true bimolecular process involving McMT and Py, perhaps involving a hydrogen bonded complex along the reaction pathway.

Several other pyridine derivatives exhibit similar abilities to facilitate the oxidation of McMT. This can be seen in Figure 7, curves a and b, which show the behavior in solutions of 3-chloro-pyridine and lutidine, respectively. It is significant that the position of the facilitated oxidation peak depends on the pK_a of the conjugate base of the pyridine derivative. This is physically reasonable, since less basic derivatives will not allow as rapid a production of McMT^- . Figure 8 shows simulations for the lutidine (curve a), pyridine (curve b) and 3-chloro-pyridine (curve c) cases. As can be seen by comparison to the data in Figures 4 and 5, the simulation produces very good agreement with the experimental data for these cases. Note that the forward rate constants for reactions 8c and 9c are not adjusted for these simulations. Rather, the entire effect of changing the basicity of the pyridine derivative is embodied in changes in the equilibrium constant for reactions 8c and 9c for the different derivatives. Note also that, as discussed above, these reactions are TSR's. Their equilibrium constants are *not* independently adjustable, but rather are fixed by those for reactions 2c, 4c and 7c. Thus, the mechanism used in the simulation is able to quantitatively fit the experimental results for a wide variety of bases using only changes in their pK_a values.

To further explore the possible involvement of bimolecular proton transfer in the facilitated oxidation of McMT by pyridine bases, the behavior of the sterically hindered base, 2,6-di-*tert*-butyl-pyridine, was examined. This base was chosen because the pK_a of its conjugate base is quite close to that of Py.^{30,35} However, it has been reported previously that this base experiences severe steric hindrance in proton transfer reactions.²¹ Thus, it was expected that proton transfer from McMT to 2,6-di-*tert*-butyl-pyridine would be inhibited. In fact, as can be seen in Figure 7, curve c, this base has absolutely no effect on the oxidation of McMT. This important result makes clear the fact that these bases are not simply acting as buffer systems that provide thermodynamic sinks for the protons generated during McMT oxidation. Rather, in order to facilitate the McMT oxidation they must be capable of a bimolecular proton transfer reaction with McMT, presumably through formation of a hydrogen bonded complex.

Conclusion

This study has described the influence of strong and weak bases on the oxidation of thiols. In particular, the comparison of experimental data with simulations shows that a unique reaction pathway involving a proton transfer between the thiol and the weak base is important in the base facilitated oxidation of the thiols. It was postulated long ago that

hydrogen bonding between amines and thiols might facilitate thiol oxidations.³⁶⁻³⁸ However, as of yet there has been no detailed mechanistic study of this process. In particular, the notion of hydrogen bonded complexes as key intermediates along the oxidation reaction pathway is quite novel. This finding is in general agreement with expectations based on previous studies of the rapid proton transfer reactions involving acids of heteroatoms.^{16-18,22,30,39} The importance of hydrogen bonding for redox processes occurring in non-aqueous solvents has been emphasized recently, especially with regard to the electrochemistry of quinones.⁴⁰

These results also bear on the mechanism by which poly(aniline) facilitates the charge and discharge of DMcT in composite cathodes formed from these materials.¹⁻⁷ Specifically, the finding that proton accepting character can dramatically alter the rates and potentials for thiol oxidations, just as proton donor character can affect the reduction of disulfides to regenerate either thiols or thiolates, suggests that the action of poly(aniline) in these composite cathode systems probably involves such proton transfer character. This importance of proton transfer may have a detrimental impact on the use of poly(aniline) to catalyze the redox processes for thiolate/disulfide redox couples in Li secondary batteries due to the adverse affect of protons in such batteries.

Acknowledgment. This work was supported in full by the Office of Naval Research.

Reference and Notes

- 1) Oyama, N.; Tatsuma, T.; Sato, T.; Sotomura, T. *Nature* **1995**, *373*, 598.
- 2) Kaminaga, A.; Tatsuma, T.; Sotomura, T.; Oyama, N. *J. Electrochem. Soc.* **1995**, *142*, 47.
- 3) Tatsuma, T.; Sotomura, T.; Sato, T.; Buttry, D. A.; Oyama, N. *J. Electrochem. Soc.* **1995**, *142*, L182.
- 4) Shouji, E.; Matsui, H.; Oyama, N. *J. Electroanal. Chem.* **1996**, *417*, 17.
- 5) Shouji, E.; Oyama, N. *J. Electroanal. Chem.* **1996**, *410*, 229.
- 6) Tatsuma, T.; Matsui, H.; Shouji, E.; Oyama, N. *J. Phys. Chem.* **1996**, *100*, 14016.
- 7) Shouji, E.; Yokoyama, Y.; Pope, J. M.; Oyama, N.; Buttry, D. A. *J. Phys. Chem. B* **1997**, *101*, 2861.
- 8) Liu, M.; Visco, S. J.; De Jonghe, L. C. *J. Electrochem. Soc.* **1990**, *137*, 750.
- 9) Murray, R. W. *Electroanalytical Chemistry Vol. 13*, p. 206, Edited by Bard, A. J., Marcel Dekker, Inc., New York and Basel **1984**.
- 10) Daum, P.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 389.
- 11) Daum, P.; Murray, R. W. *J. Electroanal. Chem.* **1979**, *103*, 289.
- 12) Simic, M.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1970**, *92*, 6096.
- 13) Hayon, E.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1972**, *94*, 7950.
- 14) Andrieux, C. P.; Saveant, J.; Tallec, A.; Tardivel, R.; Tardy, C. *J. Am. Chem. Soc.* **1997**, *119*, 2420.
- 15) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.
- 16) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1988**, *110*, 1649.
- 17) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473.

- 18) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792.
- 19) Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493.
- 20) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605.
- 21) Bernasconi, C. F.; Carre, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2707.
- 22) Parker, V. D.; Chao, Y.; Reitstoen, B. *J. Am. Chem. Soc.* **1991**, *113*, 2336.
- 23) Rudolph, M. *"Physical Electrochemistry: Principles, Methods and Applications"*, Rubinstein, I. ed.; Marcel Dekker: New York **1994**, Chapter 3, pp. 81-130.
- 24) Luo, W.; Feldberg, S. W.; Rudolph, M. *J. Electroanal. Chem.* **1994**, *368*, 109.
- 25) Fry, A. J. *"Topics in Organic Electrochemistry"*, Fry, A.J.; Britton, W.E., eds; Plenum: New York **1986**, Chap. 1, pp. 1-34.
- 26) Shouji, E.; Buttry, D. A., unpublished data.
- 27) Laviron, E. *J. Electroanal. Chem.* **1986**, *208*, 357.
- 28) March, J. *"Advanced Organic Chemistry"*, 4th Edition, Wiley: New York, **1992**, p.250, **1992**.
- 29) Kolthoff, I. M.; Chantooni Jr., M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.
- 30) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472.
- 31) Observed ^1H -NMR peaks for 3-chloro-pyridine in AN-*d*3 were 7.32, 7.80, 8.51, 8.63 ppm, those for 3-chloro-pyridine were 2.43 (methyl), 6.96, 7.4, and those for 2,6 d-di-*tert*-butylpyridine were 1.37 (methyl), 7.15, 7.58.
- 32) Pyridine peaks in IR spectrum: 3082.8, 3001.9, 1582.3, 1439.1, 1374.8, 1217.5 cm^{-1} , those for McMT: 3207.1, 2899.9, 1572.4, 1455.0, 1261.0, 1199.9 cm^{-1} , and those for McMT plus pyridine: 3207.2, 3082.8, 3001.9, 2898.1, 1582.2, 1454.1, 1439.2, 1261.1, 1200.1 cm^{-1} . The spectrum for McMT plus pyridine was the summation of those for McMT and pyridine.
- 33) Pyridine peaks in Raman spectrum: 1204.9, 1023.4, 982.4 cm^{-1} , those for McMT: 1533.8, 1247.6, 1054.6, 660.3, 542.6, 440.8 cm^{-1} , and those for McMT plus pyridine: 1533.9, 1247.7, 1055.4, 1024.9, 983.9, 657.2, 441.5 cm^{-1} . The spectrum for McMT plus pyridine was the summation of those for McMT and pyridine.
- 34) Bard, A. J.; Faulkner, L. R. *"Electrochemical Methods"*, Wiley: New York, **1980**, pp.450.
- 35) IUPAC *Ionization Constants of Organic Acids in Aqueous Solution*, Pergamon: New York **1979**.
- 36) Gilman, H. *J. Am. Chem. Soc.* **1945**, *67*, 1845.
- 37) Barnett, J. *J. Chem. Soc.* **1944**, 5.
- 38) Gabriel, S.; Colman, J. *Ber.* **1912**, *45*, 1643.
- 39) Nicholas, A. M.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.
- 40) Gupta, N.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 6384.

Figure captions

1. Experimental (upper) and simulated (lower) cyclic voltammograms for (a) 10 mM BMT with initial scan in positive direction from 0.3 V, (b) 10 mM DMcT with initial scan

negative from 0.0 V and (c) 10 mM McMT + 5 mM TEA with initial scan negative from – 0.3 V.

2. Experimental cyclic voltammograms for 10 mM BMT in solutions containing (a) no TFA, (b) 2 mM TFA, (c) 5 mM TFA, (d) 10 mM TFA and (e) 20 mM TFA. The molar ratios of [TFA]/[BMT] are shown. The initial scan in (a) is positive from 0.0 V, and in all others positive from 0.5 V.

3. Simulated cyclic voltammograms for 10 mM BMT in solutions containing (a) no TFA, (b) 2 mM TFA, (c) 5 mM TFA, (d) 10 mM TFA and (e) 20 mM TFA. All conditions as in Figure 2, except that initial scan directions are all negative starting from 1.2 V.

4. Experimental cyclic voltammograms for 10 mM McMT in solutions containing (a) no Py, (b) 2 mM Py, (c) 5 mM Py, (d) 10 mM Py and (e) 20 mM Py. Initial scan directions are all positive from –0.8 V. In (b), an additional scan with a positive limit of 0.6 V is shown that demonstrates the response from only the Py, proton-transfer-facilitated process (see text).

5. ¹H-NMR spectra in AN-*d*3 solution for 50 mM concentrations of (a) McMT alone, (b) McMT plus Py ([Py]/[McMT]=2), (c) Py alone and (d) McMT plus MSA ([MSA] / [McMT] = 2).

6. Simulated cyclic voltammograms for 10 mM McMT in solutions containing (a) no Py, (b) 2 mM Py, (c) 5 mM Py, (d) 10 mM Py and (e) 20 mM Py. All conditions as in Figure 4 except that initial scan directions are all positive from –0.8 V. In (b), an additional scan with a positive limit of 0.6 V is shown that demonstrates the response from only the Py, proton-transfer-facilitated process (see text).

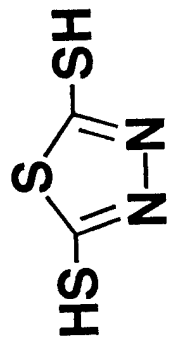
7. Experimental cyclic voltammograms for 10 mM solutions of McMT containing (a) 5 mM 3-chloro-pyridine, (b) 5 mM lutidine and (c) 5 mM 2,6-di-tert-butyl-pyridine. Initial scan directions are all positive from –0.8 V.

8. Simulated cyclic voltammograms for 10 mM solutions of McMT containing (a) 5 mM lutidine, (b) 5 mM Py and (c) 5 mM 3-chloro-pyridine. Initial scan directions are all positive from –0.8 V. All other conditions as in Figure 7.

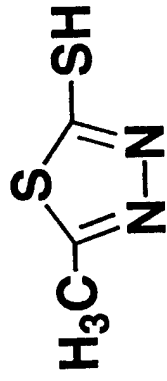
Table 1 Simulation parameters for Pyridine

No.	Electrochemical reactions			E°/V	$k_s/cm\ sec$
1e	$McMT^{+\bullet} + e^-$	\rightleftharpoons	McMT	0.85	1×10^{-3}
2e	$McMT^{\bullet} + e^-$	\rightleftharpoons	$McMT^{\ominus}$	0.14	5×10^{-3}
3e	Dimer + e^-	\rightleftharpoons	Dimer $^{\bullet-}$	-0.45	5×10^{-2}
4e	Dimer-H $^+$ + e^-	\rightleftharpoons	Dimer $^{\bullet}$ -H	0.45	1×10^{-2}
Chemical reactions					
				K_{eq}	k_f
1c	Dimer $^{\bullet-}$	\rightleftharpoons	McMT $^{\bullet}$ + McMT $^{\ominus}$	1×10^2	1×10^7 ^a
2c	McMT $^{\ominus}$ + H $^+$	\rightleftharpoons	McMT	1×10^{13} ^c	1×10^{11} ^b
3c	2 McMT $^{\bullet}$	\rightleftharpoons	Dimer	1×10^8	1×10^6 ^a
4c	McMT $^{+\bullet}$	\rightleftharpoons	McMT $^{\bullet}$ + H $^+$	1×10^{-1}	1×10^5 ^b
5c	Dimer + H $^+$	\rightleftharpoons	Dimer-H $^+$	5×10^{-1}	1×10^{10}
6c	Dimer $^{\bullet}$ -H	\rightleftharpoons	McMT $^{\bullet}$ + McMT	1×10^0	1×10^8
7c	Base + H $^+$	\rightleftharpoons	Base $^{\oplus}$ -H	5×10^8 ^d	1×10^8 ^b
8c	Base + McMT	\rightleftharpoons	McMT $^{\ominus}$ + Base $^{\oplus}$ -H	5×10^{-5} ^e	1×10^7
9c	Base + McMT $^{+\bullet}$	\rightleftharpoons	McMT $^{\bullet}$ + Base $^{\oplus}$ -H	5×10^7 ^e	1×10^9

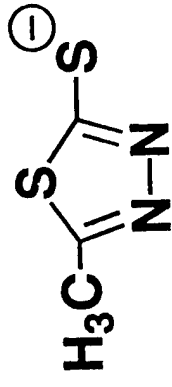
^a ref.10, 11 ^b ref.12 ^c this value was considered using pKa of triethylamine and pyridine with ref.14, 21^d 3×10^7 for 3-Clpyridine, 1×10^{10} for lutidine, and 1×10^{16} for triethylamine cases ^e thermodynamically superfluous reactions(TSR's, ref.32)



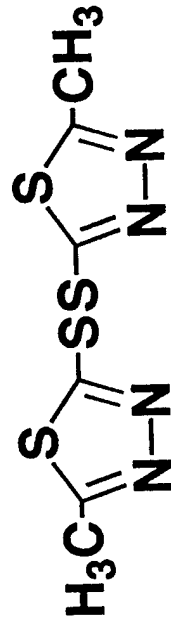
DMcT



McMT



McMT⁻



BMT

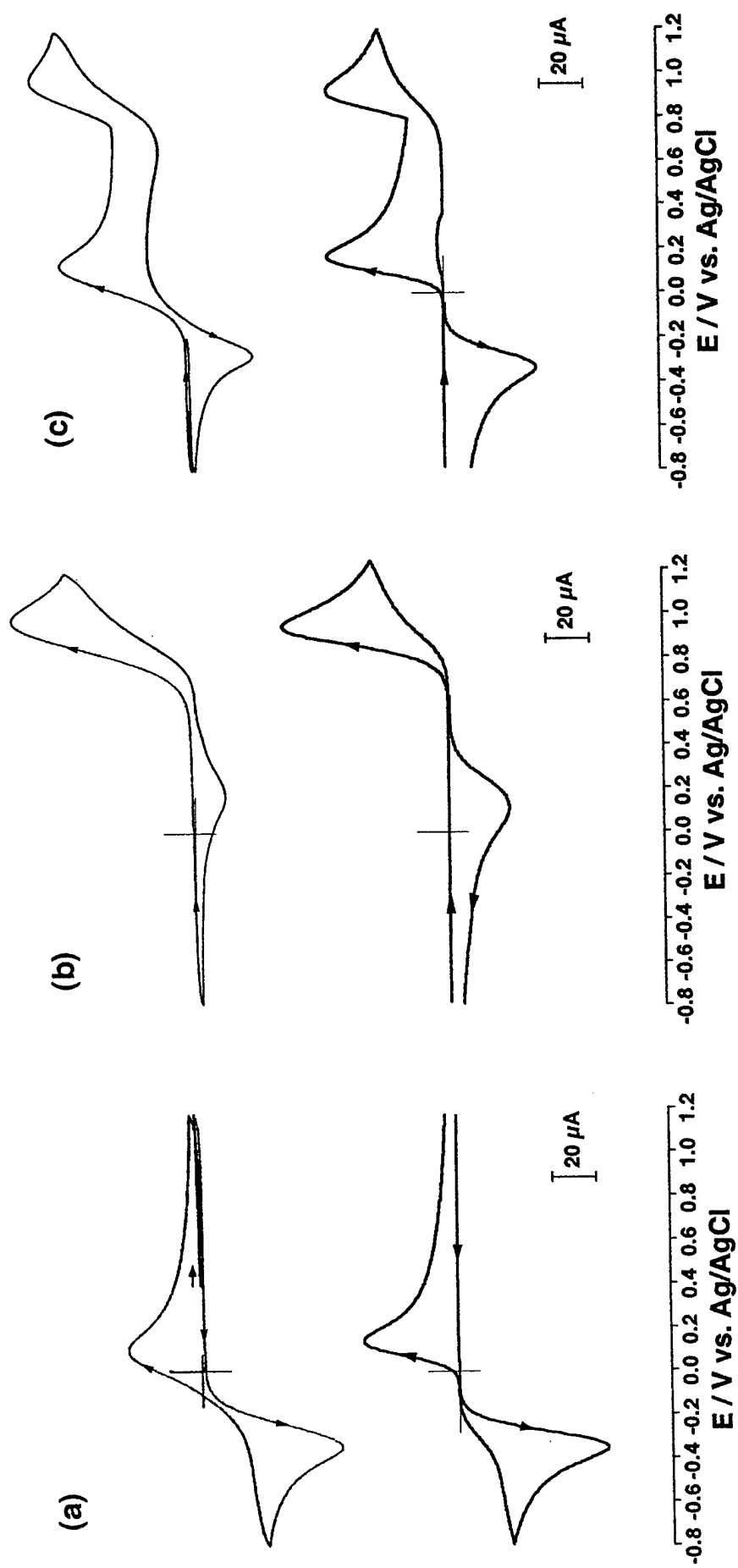


Figure 1
E Shouli and O A Ruffey

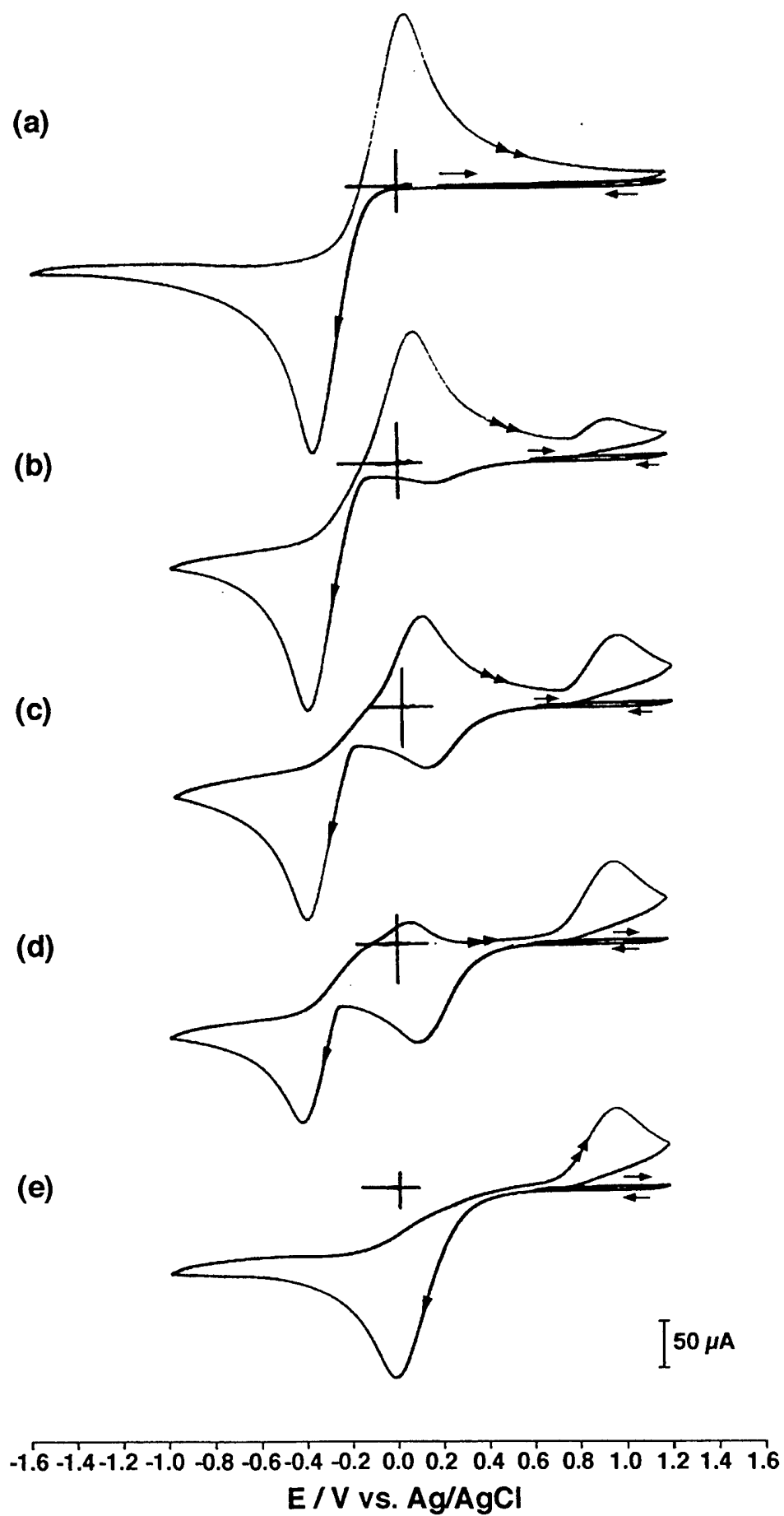


Figure 2
E. Shouji and D.A. Buttry

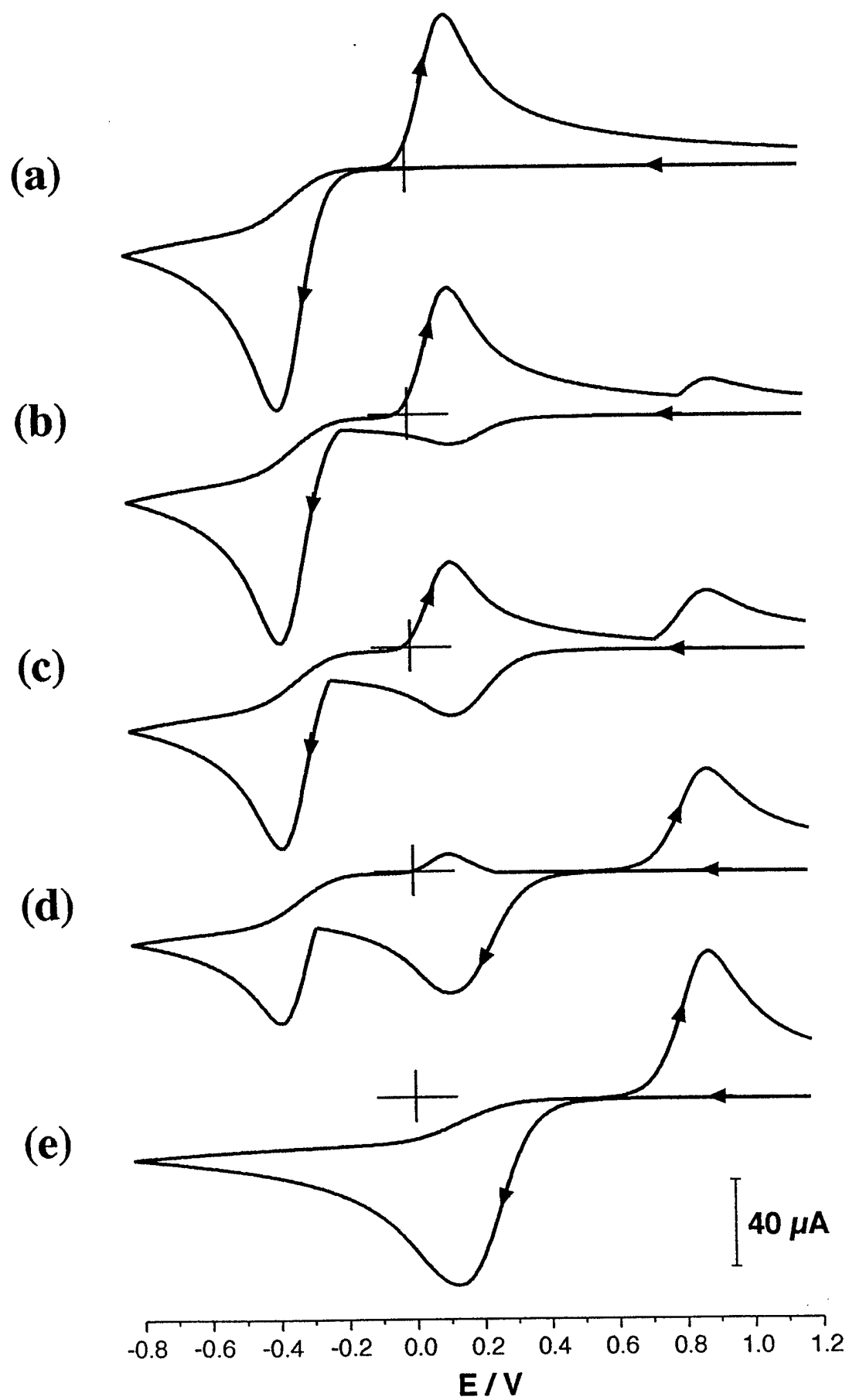


Figure 3
E.Shouji and D.A.Butry

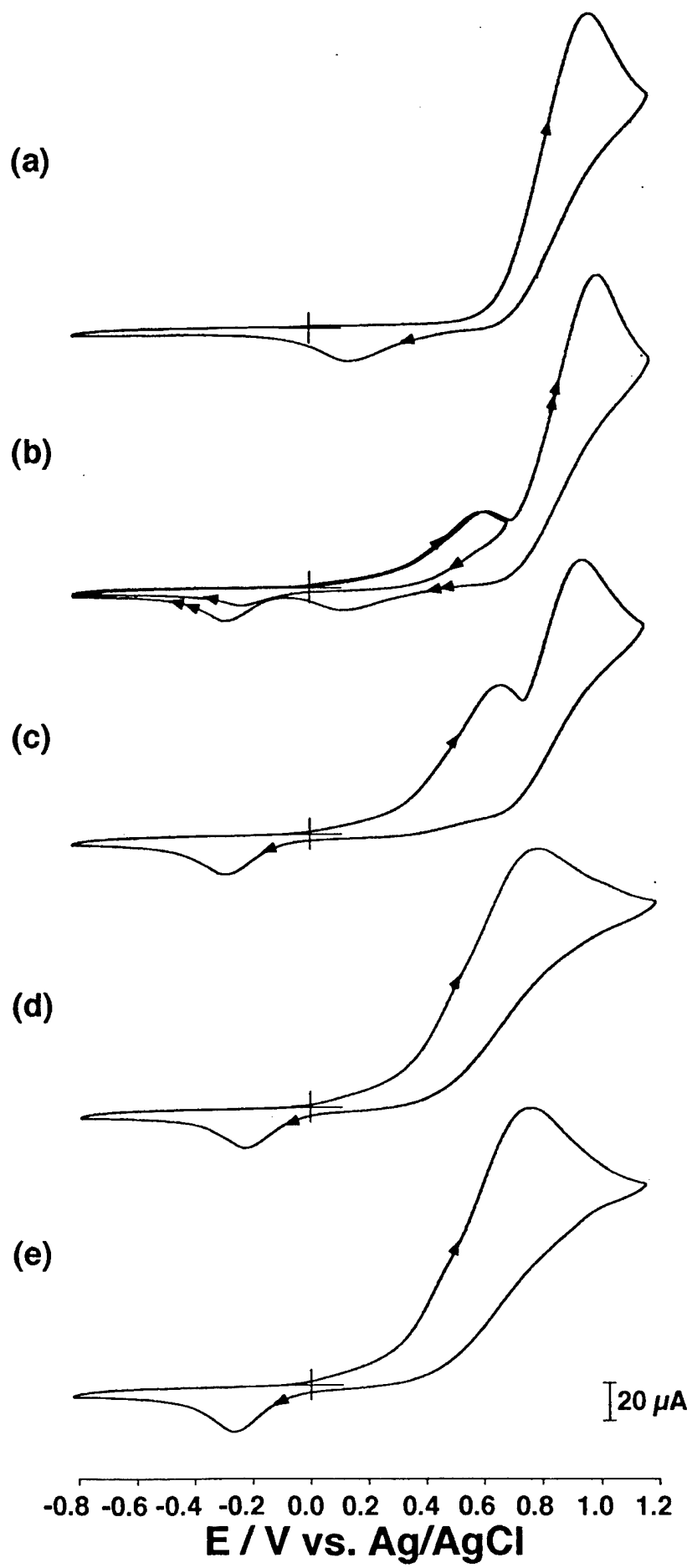


Figure 4
E. Shouji and D. A. Butry

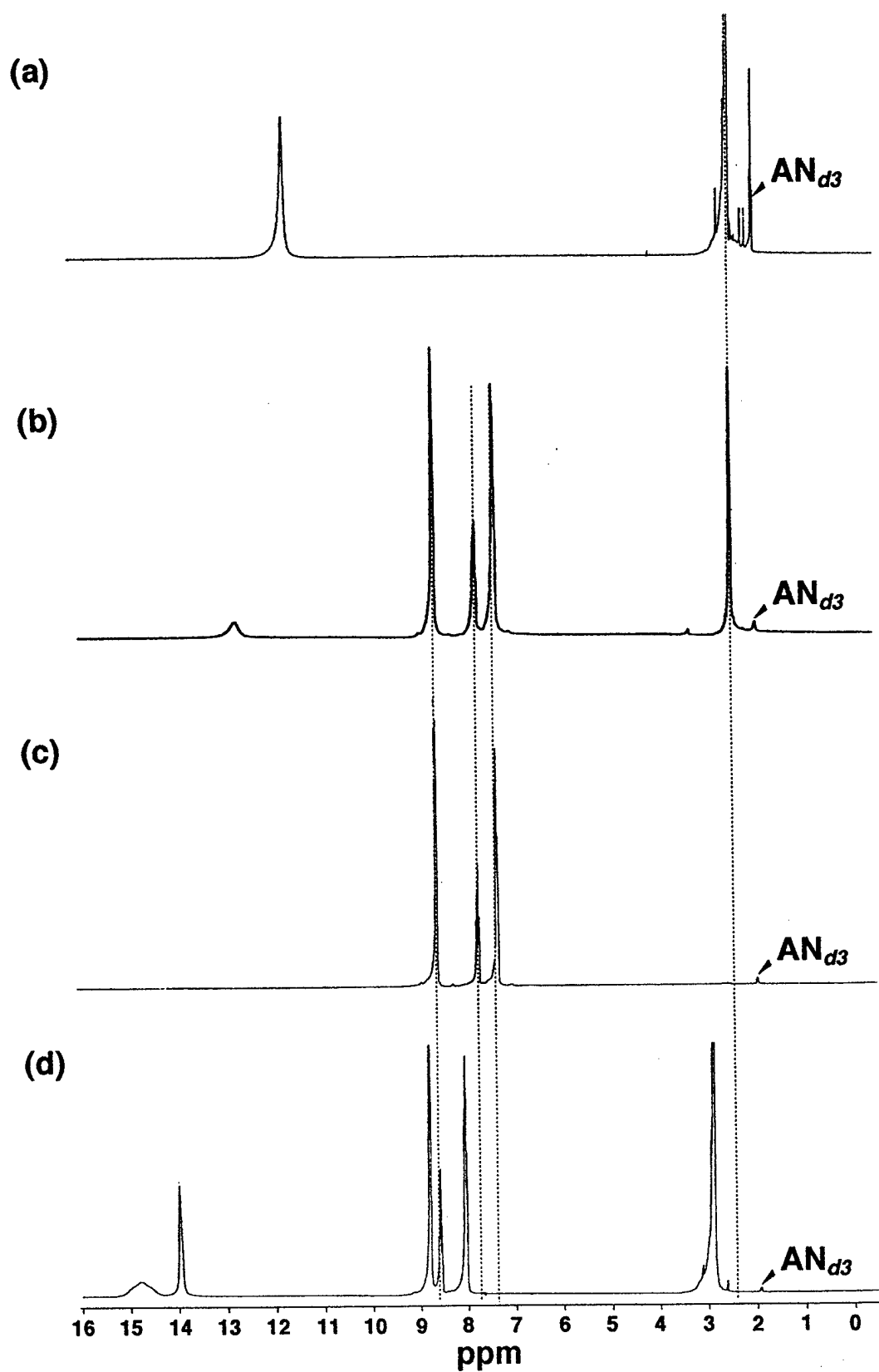


Figure 5
E.Shouji and D.A.Buttry

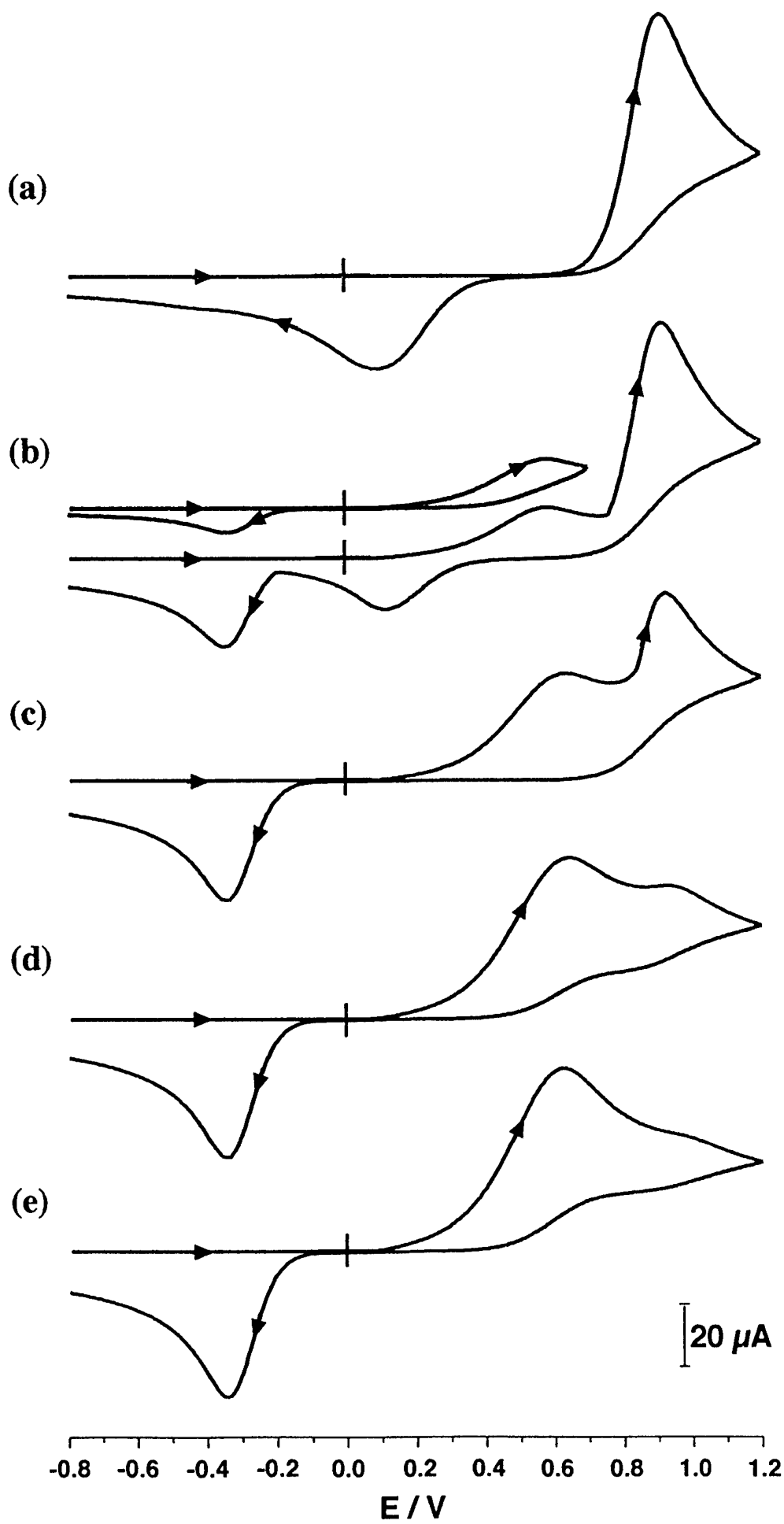


Figure 6
E.Shoufi and D.A.Butry

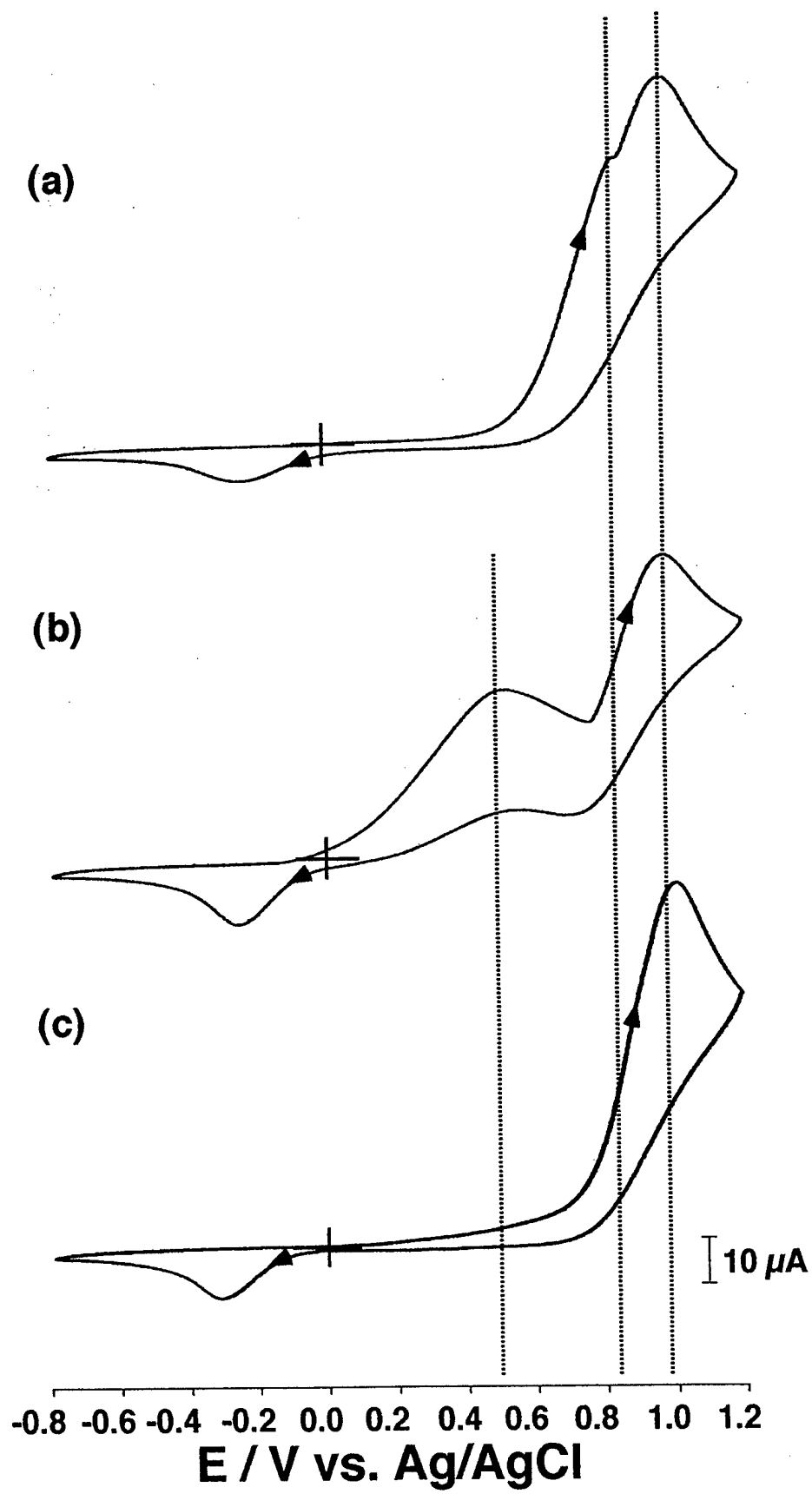


Figure 7
E. Shouji and D.A. Buttry

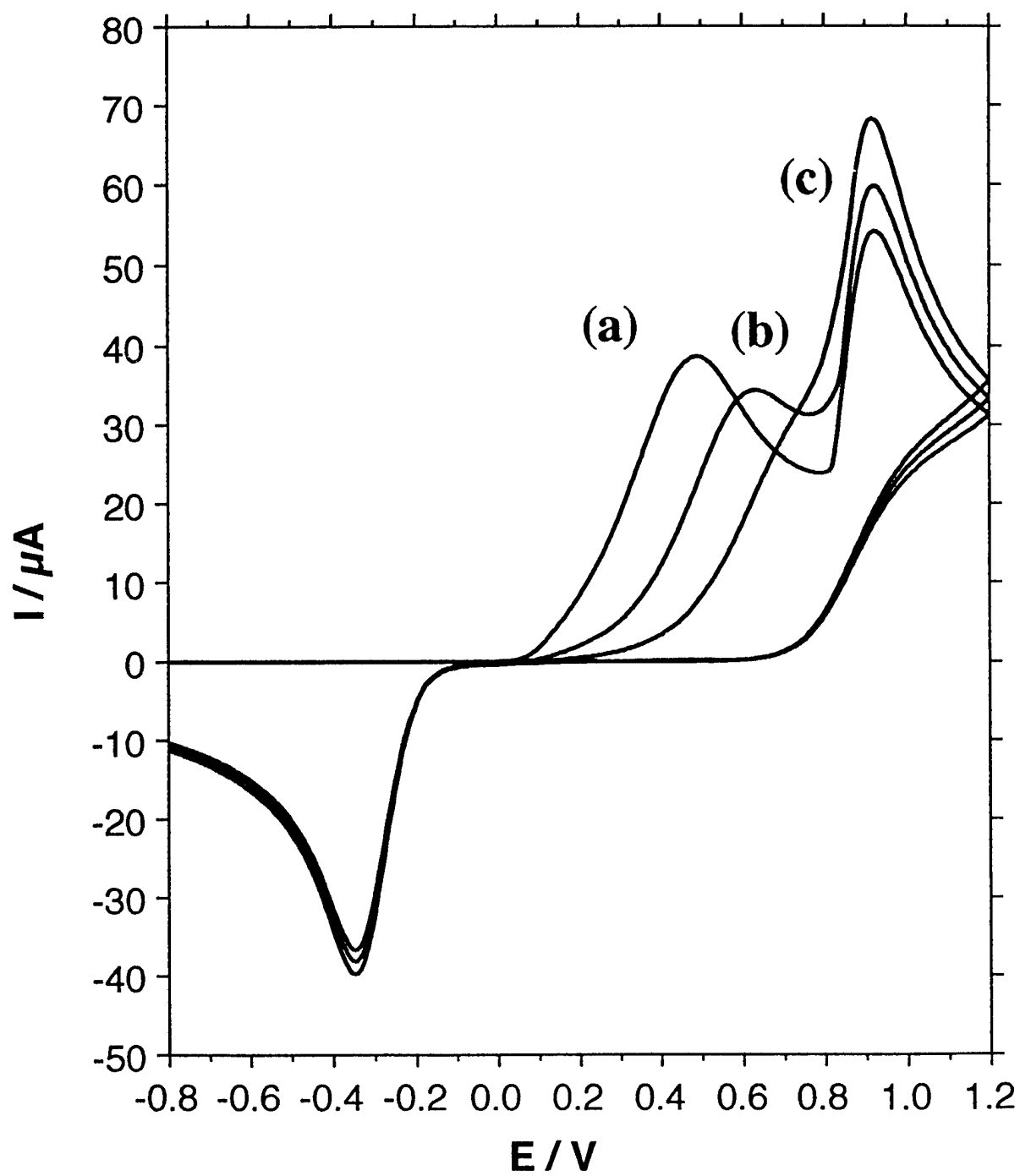


Figure 8
E. Shouji and D.A. Buttry